COPPER BASED SORBENT FOR HOT GAS CLEANUP

M. Desai, F. Brown, B. Chamberland, and V. Jalan,
ElectroChem, Inc, 400 W. Cummings Park, Woburn, MA 01801

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ABSTRACT

Coal-derived fuel gases contain significant levels of sulfur and other contaminants. Full realization of the tremendous commercial potential of coal gas fueled power plants and related technologies awaits the development of an inexpensive and reliable method for the removal of these contaminants. A family of copper manganese oxide sorbents was identified as a high temperature regenerable sulfur sorbent in the METC process. These compounds have demonstrated many advantages over other sorbents currently being studied, and there is potential for further improvement. The objectives of the development program include the study of sorbent properties such as physical characteristic, durability, temperature stability, life, rate of utilization, and development of design parameters. Copper manganese oxides provide excellent reactivity, high sulfur capacity, and complete chemical regenerability.

INTRODUCTION

For economically viable conversion of coal to electricity without significant loss of thermal energy, there is a need to reduce sulfur from coal gas stream at high temperatures, 500-800°C.[1] A capability for efficient removal of sulfur is essential for integration of coal gasifiers with synthesis gas catalytic conversion processes (methanol, methane, Fischer- Tropsch) and power plants such as gas turbine combined cycle and molten carbonate fuel cells. Over the past decade there have been extensive efforts by DOE/METC and its contractors to define appropriate high temperature regenerable desulfurizing agents,[2,3] since there are both technical and economic advantages for the desulfurization of coal gas fuel and fossil fuel flue gases by hot dry scrubbing. Successful sorbents should provide efficient desulfurization and regeneration kinetics, a reduction to H_2S of 1 ppm level, and physical and chemical stability in both desulfurization and regeneration gas atmospheres at a temperature of 500°C and above.

Mixed metal oxides are recent experimental high temperature sulfure sorbents. They provide some outstanding properties for hot regenerative desulfurization of coal gases. Although quite promising results have been obtained for hot desulfurization of coal gases with these sorbent systems, they have limitations.

Zinc ferrite[3-5] shows great potential and remains the sorbent of choice. Its sulfur capacity is relatively high and it is moderate in cost. The disadvantages are degradation due to thermal sintering, sulfate formation, and zinc volatilization. Copper zinc oxide[6-9] has been investigated as a very low level H_2S sorbent. It was shown that copper in a mixed oxide state retains the thermodynamic properties of cuprous oxide and indeed reduced sulfur levels below 1 ppm at 650°C. This was subsequently verified by several other METC supported projects.[10] Copper zinc oxide is expected to suffer from some of the same drawbacks as zinc ferrite. However, these led to many investigation of copper based mixed oxides. Manganese oxide has been reported to be a potential candidate for high temperature desulfurization.[11-14] Its rate of reaction with hydrogen sulfide is four times faster than that of zinc oxide.[12] Air regeneration, unfortunately, leads to sulfate formation. It appears that Cu_2O-MnO based sorbents will eliminate many of the deficiencies.

EXPERIMENTAL SECTION

Reactor System and Experimental Procedures

The reactor, used is an 18 inch long stainless steel tube with a 1 inch I.D. quartz liner. The first 10 inches of the reactor are filled with an inert porcelain packing to promote the heating of the inlet gases. Sorbents are placed on a stainless steel mesh retainer directly above this section. The reactor is mounted vertically inside an electric furnace and equipped with two K-type thermocouples which can be moved along the central axis. N_2, H_2, CO, CO_2, and H_2S are individually metered through mass flow controllers and the desired concentration of water vapor is attained by injecting water via a metering pump. The experiments consisted of a sequence of alternate sulfidation and regeneration runs. The reactor temperature was held fixed in the range of 500-800^oC for the duration of the experiments. Sulfided sorbents were regenerated with air and nitrogen at 500-750^oC. The space velocity of gas used was in the range of 1000-2000 hr^{-1} during sulfidation and 600-800 hr^{-1} during regeneration.

Matheson-Kitagawa precision gas detection tubes were used to determine the concentrations of H_2S, CO_2, and SO_2 in the inlet and effluent stream. Our previous experience shows that this technique is accurate and cost effective.[2,6-9] Semi-quantitative methods were devised for the continuous monitoring of the effluent gas stream for H_2S during desulfurization and SO_2 during regeneration.

Sorbent Preparation

Several methods for synthesizing highly dispersed mixed oxides are described in the literature.[15-16] The method selected for evaluation in this study is coprecipitation of inorganic salts. The development of technique for the production of low-cost finished sorbent is a long term objective of the program. The copper-manganese oxides were coprecipitated from aqueous nitrate solution by the addition of NaOH. The precipitate was recovered by filtration and washed with distilled water to remove soluble residues. The recovered mixed hydrous oxides were dried in air at 100^oC. Sorbents with copper to manganese weight ratios of 90:10, 80:20, 75:25, 60:40, 54:46, 50:50, 40:60, 37:67, and 20:80, were prepared. Pure manganese oxide was also prepared by precipitation.

Sulfidation and Regeneration Studies

The H_2S concentration in the effluent rises rapidly when the sorbent has reached its sulfur capacity. This abrupt change is called the breakthrough; the elution profile is called an uptake curve. In the absence of transport and kinetic limitations, the uptake curve would be the step function $y = y^{eq}$ at $t < t^*$, $y = y^o$ at $t > t^*$ where y^{eq} and y^o are the equilibrium and inlet mole fractions of hydrogen sulfide, respectively, and t^* is the theoretical time corresponding to complete sulfidation of the active sorbent components. The results are presented in terms of the concentration of H_2S in the product gas versus the normalized time t/t*. In the case of successive sulfidations, the uptake curve cycles are denoted 1, 2, etc. Regeneration was carried out in air at 650°C, and an overnight N_2 purge at 750°C followed.

Results and Discussion

Sulfur loadings at 20 ppm and 100 ppm concentration in exit gas stream were estimated from the weight of sorbent, gas feed rate, and time to breakthrough. Figure 1 summarizes the effect of manganese content in the $Cu_xMn_yO_z$ system on the sulfur loading of the resulting sorbent. As expected, the performance of pure copper oxide is very poor. Incorporation of manganese oxide dramatically increases the sulfur loading capacity; this is attributed by the stabilization of cuprous oxide.[7] Pure manganese oxide has a high sulfur capacity but lacks regenerability. Of interest is the decrease in sulfur capacity at the $CuMnO_2$ phase and a minimum at $CuMn_2O_4$ phase.[17]

Figure 2 shows the breakthrough curve of six sulfidation cycles of the sorbent with a copper to manganese atomic ratio of 1:1. The sulfur loading after the first cycle (19 weight percent at 20 ppm breakthrough) was in agreement with our previous results.[17] The constant H_2S leakage rate of less than 30 ppm in the effluent was observed in subsequent cycles.

A single sulfidation test of freshly prepared sorbent $CuMnO_2$ was carried out in the 1 inch dia. reactor at 550, 600, 650, 700, 750, and 800°C. A constant space velocity of 2000 hr^{-1}, and simulated fuel gas mixture (feed gas) consisting of on dry basis 47% N_2, 27% H_2, 15% CO_2, 10% CO and 1% H_2S was used. Sorbent loadings are presented in figure 3. It is clear that use of the $CuMnO_2$ sorbent at low temperatures (550-600°C) gives longer breakthrough times than at higher temperatures. Sulfur loadings of the $CuMnO_2$ sorbent at 550°C was 28% at 20 ppm breakthrough, with decreasing loadings at higher temperatures, to 1.6% at 800°C. An H_2S leakage rate of less than 20 ppm was obtained only for a short period of time (i.e. high loadings on the sorbent) only at temperatures of 650°C and below, but leakage rates below 50 ppm were obtained over extended temperature range.

The primary conclusion from these tests is that a copper-manganese oxide sorbent with a Cu to Mn 1:1 atomic ratio will perform best at relatively low temperatures, preferably in the range of 550-600°C.

Figure 4 presents the results of copper-manganese oxide sorbent with a Cu to Mn 1:2 atomic ratio. The test conditions for the sulfidation cycles were same as mentioned above. The sulfur loadings were low, and short breakthrough times were observed for the tests performed at 550 and 600°C. The sulfur loadings improved as the sulfidation temperature increased. In all cases the breakthrough time for less than 40 ppm H_2S exit concentration were relatively short. A sulfur loading of 24% was observed at 50 ppm and 750°C. The sulfidation test at 800°C showed a sulfur capacity reduced by half at 50 ppm breakthrough. The primary conclusion from tests is that a sorbent riches in manganese content performs better at relatively higher temperatures preferably in the range of 700-750°C, than sorbents with lower manganese content.

The results presented in figures 3 and 4 show that in both cases the sulfur loading decreased drastically at 800^{o}C. These results suggest that it would be more advantageous to operate both sulfidation and regeneration cycles below 800^{o}C to increase loadings and decrease loss of activity due to sintering or other processes that result in loss of mechanical integrity.

Additional sulfidation tests of a sorbent with copper to manganese stoichiometric ratio of 1:1 were carried out at 650^{o}C and spacevelocity 2000 hr^{-1}, with various inlet H_2S concentrations, ranging from 500 ppm to 1 %. Sorbent loadings under these conditions are shown as figure 5. The sulfur capacity was highest at 500 and 1000 ppm and decreased at 5000 ppm and 1% inlet H_2S concentrations. Duplicate test with 5000 ppm showed the same breakthrough time. The reason for the relatively low sulfur capacity at higher inlet H_2S concentrations is not clear. Since the sulfur loadings reported here are for relatively low H_2S exit concentrations (20-100 ppm) the sulfur loadings are not associated with equilibrium values. With high inlet H_2S concentrations a small amount of channeling through the reactor bed would explain the apparently anomalous behavior.

Figure 6 shows sulfur loadings of sulfidation tests of fresh sorbent copper manganese oxide with a Cu to Mn stoichiometric ratio of 1:1 at various inlet water concentrations ranging from 0 to 30%. The sulfur capacity decreases with an increase in the water content of feed gas. The mixed metal oxides reacts with H_2S producing metal sulfides and water. As the partial pressure of water increases in the feed gas, the reaction becomes more equilibrium limited, resulting in higher H_2S leakage in the effluent.

The $CuMnO_2$ sorbent prepared in 1/16" pellet form by the coprecipitation method was sulfided at 650^{o}C for about 10 hours in the presence of a simulated coal gas mixture containing N_2 47.07%, H_2 27.3%, CO_2 14.3%, CO 10.4%, and H_2S 0.93%. The sulfided sample was cooled to room temperature under N_2 and small portions of the sulfided sample were regenerated individually in air at various temperatures in the range of 650-950^{o}C. Samples were also regenerated by thermal decomposition in a mixture of N_2 and steam at 850^{o}C. These samples were analyzed by XRD.

The sulfided sample of copper manganese oxide sorbent regenerated in air at 650 and 700^{o}Cshowed a spinel phase. The samples regenerated at 750, 850 and 950^{o}C showed mixed phases containing both CuO and spinel. The sample regenerated by thermal decomposition at 850^{o} showed a mixture of MnO, Cu metal and trace amount of spinel. None of the samples regenerated at the above conditions showed any sulfate formation.

Another set of experiments was carried out using pure, single phase $CuMnO_2$. The sample was prepared from low surface area technical grade Cu_2O and Mn_2O_3 mixed in a 1:1 ratio and pelletized. A single tablet of pure $CuMnO_2$ was sulfided at 650^{o}C for 2 hours. A half tablet from the sulfided sample was regenerated at 650/750^{o}C in air/N_2. These samples were analyzed by XRD. The surface of the sulfided sample showed mostly $MnS_{1-x}O_x$, whereas the regenerated sample showed strong CuO. The presence of the $MnS_{1-x}O_x$ phase indicates that sorption proceeds through a more complex mechanism than would be inferred from a simple description of the stoichiometry of the overall reaction.

Conclusion

Copper and manganese form stable oxide phases, that are easily sulfided and regenerated back to $CuMnO_2$ and $CuMn_2O_4$. These results were verified by desulfurization/regeneration studies as well as chemical and XRD analysis of fresh, sulfided, and regenerated sorbents. Very advantageously, copper manganese sulfate exists only as a hydrated material, campigliaite, which is so unstable that it decomposed under the electron beam during microprobe studies.[18-19] Unlike those of zinc, copper and manganese compounds are stable and do not volatilize at temperatures of interest.

Sorbents with Cu to Mn 1:2 atomic ratio have the highest sulfur capacity at higher temperature, while the sorbent with Cu to Mn 1:1 atomic ratio have the highest sulfur capacity at lower temperature. Loading capacity is influenced by water content, as expected, but the results are not too sensitive to water content in the 20-30% H_2O range at 650°C.

We have demonstrated that copper manganese oxides are attractive candidates for high temperature regenerable sulfur sorbents. The absence of sulfate formation, very low thermal sintering below 650°C, provide incentive to pursue further development of this process.

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FIG.1 SULFUR LOADING OF COPPER BASED SORBENTS

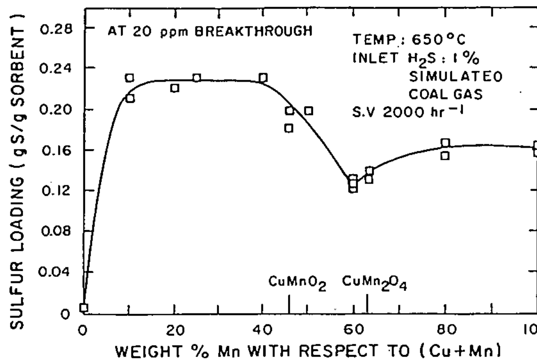

FIG.2 H_2S BREAKTHROUGH CURVES FOR $CuMnO_2$

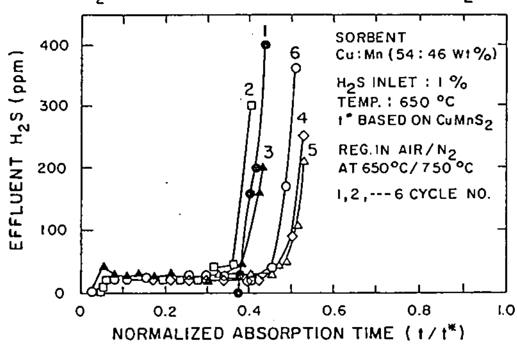

FIG.3 SULFUR CAPACITY VS. SULFIDATION TEMP.
($CuMnO_2$ 1/16" PELLETS)

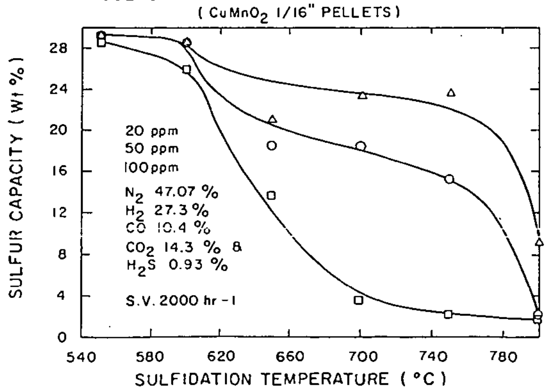

FIG. 4 SULFUR CAPACITY VS. SULFIDATION TEMP.
($CuMn_2O_4$ 1/16" PELLETS)

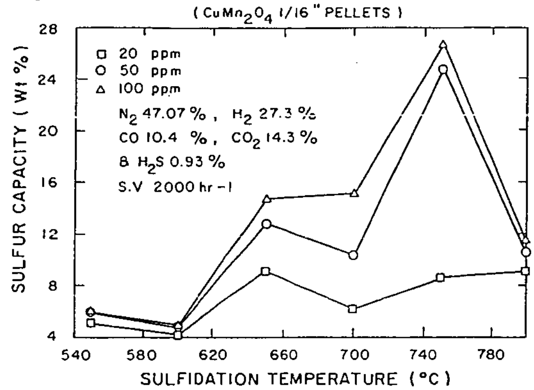

FIG. 5 SULFUR CAPACITY VS. INLET H_2S CONC.

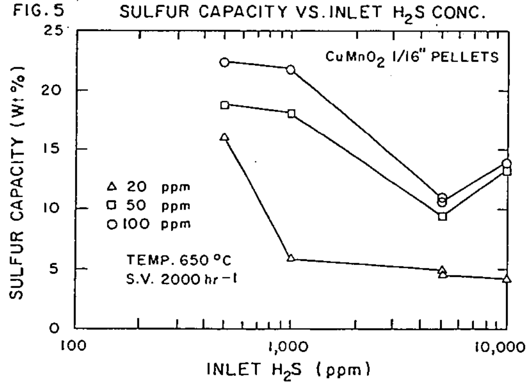

FIG. 6 SULFUR CAPACITY VS. INLET WATER CONC.
($CuMnO_2$ 1/16" PELLETS)